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COMPLETE SPECIFICATION

Process for the manufacture of Water-Repellent Fabricated Shaped Structures and Coatings made from Inorganic Compositions

We, WACKER-CHEMIE, G.m.b.H., a Company recognised by German law, of 8 München, 22, Prinzregentenstrasse 22, Germany, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention provides a process for the manufacture of water-repellent fabricated shaped structures and coatings made from inorganic compositions that harden when water is added, the water-repellency being achieved by the use of organosilicon compounds.

The usefulness of compositions that harden when water is added, especially gypsum, is limited by the considerable capacity of articles made therefrom to absorb and by the marked water-solubility of the said articles. It has therefore been proposed to reduce the sensitivity to water of such articles by the use of organosilicon compounds that impart water repellency. Either the compounds have been added to the compositions that harden when water is added prior to the shaping process or the finished articles have been coated with the said compounds. However, the degree of water-repellency achieved with the organopolysiloxanes hitherto used in the field of building materials is inadequate. Trials have also been carried out with alkaliorganosiliconates, but the disadvantage of these products is that they are liable to be washed out before they can develop their full effect and that they sometimes cause efflorescence.

The present invention provides a process for the manufacture of water-repellent fabricated shaped structures and coatings made from inorganic compositions that harden when water is added, to produce articles having a higher degree of water-repellency than those manufactured with the aid of the organopolysiloxanes used hitherto in the field of building materials and not having the disadvantages associated with the use of alkaliorganosiliconates as agents conferring water-repellency.

In the process of the invention the water-repellency is achieved by the addition of organosilicon compounds in the form of aqueous emulsions to the inorganic compositoins prior to the shaping process, the organosilicon compounds used being organopolysiloxanes prepared from 2 to 100 mol per cent of units of the general formula $R_xSiH_mO_{\frac{4-m-x}{2}}$, in which R represents an alkyl radical having 1 to 4 carbon atoms, x represents 0, 1 or 2, on average 0.7 to 1.3 m represents 1, 2 or 3 and the sum of $m + x$ is 1, 2 or 3, and 0 to 98 mol per cent of units of the general formula $R_nSiO_{\frac{4-n}{2}}$, in which R has the meaning given above and n represents 0, 1, 2 or 3 and on average is 0.9 to 1.8; and the ratio of the sum of the silicon-bonded hydrogen atoms to the sum of silicon atoms in both kinds of siloxane unit is 0.02 to 1.25.

The process of the invention is specially suitable for the manufacture of fabricated shaped structures and coatings from inorganic compositions that harden when water is added, which compositions have a pH value below 7.5 in the aqueous medium prior to hardening, in other words, compositions that are acid or neutral. Of the acid and neutral compositions of the kind defined that come within the scope of the invention special mention may be made of gypsum. Articles made from gypsum that has not been treated in accordance with the process of the invention are specially sensitive to water and therefore the process of the invention has very great advantages to offer in respect of the manufacture of articles made

from gypsum. Unlike Portland cement, for example, which is a water-resistant binder, that is to say, a hydraulic binder, gypsum belongs to the group of binders that are not resistant to water, that is to say, non-hydraulic binders. The efficiency of the process of the invention is specially surprising in the case of gypsum because this substance generally does not contain an alkali that could liberate the silicon-bonded hydrogen and promote the condensation of the silicon-bonded hydroxyl groups thereby formed.

Of the various kinds of gypsum available, preference is given to plaster ($CaSO_4.1/2\ H_2O$) in the form of, for example, gypsum plaster, stucco plaster or insulating plaster. If desired, however, the process of the invention can be applied to flooring plaster, Keene's cement, anhydrite and mixtures of plaster and hydrated time. The gypsum may contain the usual additives, for example, sulphate accelerators, thinning agents, for example, sulphite waste liquor powder, dyestuffs, pigments, setting retarders, fillers or reinforcing agents, for example, sand, calf hair, wood fibres, synthetic fibres, asbestos fibres, vermiculate (exfoliated mica) or perlite, or blowing agents.

Also included in the group of inorganic compositions that harden when water is added and that have a pH value below 7.5 in aqueous medium prior to hardening are binders based on magnesium oxide and magnesium chloride, for example, Sorel's cement. The process of the invention can also be applied to binders of this kind, although preference is given to gypsum.

If desired, the process of the invention can also be applied to other inorganic substances that harden when water is added, for example, lime (CaO), Portland cement and aluminous cement ($CaO.Al_2O_3$).

Like gypsum, the other inorganic substances that harden when water is added can be processed in the presence of the usual additives, for example, the additives used when they are being made into mortar or structural units, for example, artificial stones and wall tiles. Such additives are, especially, sand, sawdust and wood-wool.

The manufacture of fabricated shaped structures and coatings from substances that harden when water is added has been known for a long time. The measures adopted in the process of the invention can be the same with the exception that use is made of the aqueous organopolysiloxane emulsions of the type defined above.

The radical R in the formulae given hereinbefore may be a methyl, ethyl, n-propyl, isopropyl, n-butyl or secondary butyl radical. The radicals R bound to a single silicon atom may be identical, as in dimethyl siloxane units or they may be different as in ethylmethyl siloxane units, or different radicals R may be bound to the different silicon atoms of the organopolysiloxanes. Preferably, at least 80 per cent of the radicals R are methyl radicals.

Advantageously, the average value of x is 0.9 to 1.0 and the average value for n is 0.9 to 1.2; the ratio of the sum of the silicon-bonded hydrogen atoms to the sum of silicon atoms in the two kinds of siloxane units is preferably 0.1 to 1.0.

The organopolysiloxanes of the kind defined above that are used in the process of the invention may be copolymers of siloxane units that contain no silicon-bonded hydrogen and siloxane units that contain silicon-bonded hydrogen, mixtures of organopolysiloxanes that contain no or practically no silicon-bonded hydrogen, these being, by virtue of the R/Si ratios indicated above, so-called "organopolysiloxane resins", and organopolysiloxanes that contain silicon-bonded hydrogen in some or all of the siloxane units, or organopolysiloxanes that contain silicon-bonded hydrogen in all siloxane units alone. Preference is given to mixtures comprising organopolysiloxanes containing silicon-bonded hydrogen and organopolysiloxanes that are free, or virtually free from silicon-bonded hydrogen, the reason being that they are easy to obtain and that it is easier to produce a specific ratio of siloxane units containing silicon-bonded hydrogen to siloxane units that do not contain silicon-bonded hydrogen.

Of the organopolysiloxanes used in accordance with the invention, at least those that are free from silicon-bonded hydrogen or that are preferably free from silicon-bonded hydrogen, preferably contain not more than 25 mol per cent of siloxane units having 2 or 3 silicon-bonded organic radicals per molecule and, in the water-free state, they advantageously have a viscosity not exceeding in 1,000 cSt at 25°C (measured in 50 per cent by weight toluene solution).

Since it is important that the organopolysiloxanes used in the process of the invention be in the form of aqueous emulsions as well as having a content of silicon-bonded hydrogen, 1 to 20 percent of the siloxane oxygen atoms may be replaced by hydroxyl groups and/or alkoxy groups of the general formula OR, in which R has the meaning given above. This applies in particular to the organopolysiloxanes that are free from, or practically free from, silicon-bonded hydrogen in mixtures containing such organopolysiloxanes.

The organopolysiloxanes used in the preparation of the emulsions to be used in the process of the invention are preferably prepared by the joint or separate hydrolysis of the corresponding halogen-silanes, for example, methyltrichlorosilane or methyldichlorosilane, if necessary, after a proportion of the halogen atoms has been replaced by groups of the formula RO, in which R has the meaning given above, in the presence of an organic solvent, for example, toluene. Processes of this

kind are known.

The preparation of aqueous emulsions of organopolysiloxanes is generally known, and the preparation of the emulsions to be used in the process of the invention can be carried out by these known methods.

If necessary, the dispersing agents normally used in the preparation of aqueous organopolysiloxane emulsions may also be used in the preparation of the organopolysiloxane emulsions to be used in the process of the invention. Examples of suitable dispersing agents are protective colloids, for example, polyvinyl alcohol, which may contain up to 40 mol per cent of acetyl groups, gelatine and cellulose derivatives, for example, water-soluble methyl cellulose; annion active emulsifiers, for example, alkali metal and ammonium salts of long-chain fatty acids, organic sulphonic acids or acidic sulphuric acid esters, for example, sodium laurate, sodium isopropylnaphthalenesulphonate, sodium dioctylsulphosuccinate, triethanolammonium oleate and sodium lauryl sulphate; cationic emulsifiers, for example stearylammonium chloride, and non-ionic emulsifiers, for example, sorbitol monolaurate and polyhydroxyethylene ethers of monohydric or polyhydric aliphatic alcohols or aromatic hydroxy compounds. Non-ionic emulsifiers are preferred. The dispersing agents are advantageously used in amounts of 0.1 to 5 per cent by weight, based on the weight of organopolysiloxanes used.

In the preparation of the organopolysiloxane emulsions used in the process of the invention the liquid organopolysiloxanes may be used in the solvent-free form or in the form of solutions in organic solvents that are liquid under normal conditions. Preferably, the emulsions are prepared from solutions of the organopolysiloxanes. Examples of suitable organic solvents are aliphatic and aromatic hydrocarbons, for example, petroleum fractions boiling in the range of 130° to 220°C, or toluene; chlorinated hydrocarbons, for example, trichloroethylene; esters, for example, methyl acetate; ethers, for example, di-n-butyl ether, and ketones, for example, methylethyl ketone. The organic solvents are advantageously used in amounts of 25 to 75 per cent by weight, based on the weight of organopolysiloxanes used.

The organopolysiloxane emulsions to be used in the process of the invention advantageously contain 0.001 to 50 per cent by weight of organopolysiloxane, based on the weight of the emulsion. The water content of the emulsions will depend on the proportion of organopolysiloxane and any dispersing agent or solvent that is also present.

Organopolysiloxane emulsions of the kind defined tend to evolve hydrogen on storage. It may therefore be advantageous to add a small amount of an organic acid, for example, acetic acid, or an aldehyde, for example, acetaldehyde, to the emulsions in order to reduce or prevent the evolution of hydrogen.

The amount of organopolysiloxane used is preferably 0.001 to 10 per cent by weight, especially 0.02 to 2 per cent by weight, based on the dry weight of inorganic substances that hardens in the presence of water and depends on the content of silicon bonded hydrogen in the organopolysiloxanes. As has already been mentioned the organopolysiloxane emulsions to be used in accordance with the invention are added to the inorganic substances prior to the shaping process. It is advantageous to add the organopolysiloxane emulsions to the mixing water, that is to say, the water used to harden the inorganic composition, or to use organopolysiloxane emulsions of an appropriately low concentration as the mixing water, which is the simplest possible method of ensuring uniform distribution of the emulsion within the inorganic substance to be hardened.

It is not necessary to use hardening catalysts and in fact such catalysts are preferably not used in the process of the invention.

The water-repellent action of the additives used in accordance with the invention is displayed as soon as the inorganic substance, for example, gypsum, has hardened. No deleterious effect on flexural strength or compressive strength of the shaped articles has been observed.

The following Examples illustrate the invention:

EXAMPLE 1

80 grams of a liquid organopolysiloxane comprising about 80 mol per cent of monomethylsiloxane units and 20 mol per cent of dimethylsiloxane units with 8 per cent by weight of ethoxy groups and 6 per cent by weight of silicon-bonded hydroxyl groups and 20 grams of a methylhydrogen polysiloxane having a viscosity of 25 cSt at 25°C, prepared by pouring a 30 per cent by weight solution of methylene dichlorosilane (CH_2SiHCl_2) in toluene into five times the amount by weight of water and distilling the toluene out of the organic layer, were dissolved in 100 grams of toluene. The solution so prepared was emulsified in 299 grams of water to which 1 gram of a commercially available nonylphenylpolyoxyethylene ether had been added as emulsifier (Emulsion A).

Emulsion B, serving as control, was prepared in the same manner with the exception that the organopolysiloxane mixture described above comprising 80 grams of organopolysiloxane free from silicon-bonded hydrogen and 20 grams of organopolysiloxane containing silicon-bonded hydrogen was replaced by 100 grams of an organopolysiloxane resin free from silicon-bonded hydrogen and comprising monomethyl siloxane units and dimethyl siloxane units.

A number of 50 gram portions of gypsum

plaster prepared by heating gypsum — $CaSO_4.2H_2O$ — to 180°C to 700°C) were each mixed with 35 grams of a mixture comprising water and different amounts of either Emulsion A or Emulsion B. The mixtures so prepared were poured into metal dishes. After one hour the water-repellency of the plaster discs so obtained was assessed by measuring the rate at which drops of water (0.5ml each) penetrated the material. The following results were obtained:

TABLE I

Emulsion used	Per cent by weight of emulsion, based on dry plaster	Rate of penetration in seconds
—	—	6
A	0.5	5400
A	1.0	7380
A	2.0	11880
A	4.0	16980
B	1.0	13
B	2.0	15
B	4.0	78

EXAMPLE 2

An emulsion was prepared in the manner adopted for Emulsion A in Example 1, with the exception that 60 grams of organopolysiloxane free from silicon-bonded hydrogen was used instead of 80 grams, and that 40 grams of methyl-hydrogen polysiloxane was used instead of 20 grams. The preparation of the plaster discs and assessment of their water-repellency were carried out in the manner described in Example 1, the following results were obtained:

TABLE II

Per cent by weight of emulsion, based on dry plaster	Rate of penetration in seconds
0	7
0.2	168
2.0	19500

EXAMPLE 3

An emulsion was prepared in the manner adopted for Emulsion A in Example 1, with the exception that 90 grams of organopolysiloxane free from silicon-bonded hydrogen was used instead of 80 grams, and that 10 grams of methyl-hydrogen polysiloxane was used instead of 20 grams. The preparation of the plaster discs and assessment of their water-repellency were carried out in the manner described in Example I. The following results were obtained:

TABLE III

Per cent by weight of emulsion, based on dry plaster	Rate of penetration in seconds
0	7
0.2	28
2.0	3420

WHAT WE CLAIM IS:—

1. A process for the manufacture of water-repellent fabricated shaped structures and coatings from inorganic substances that harden when water is added, wherein there is added to the inorganic substance prior to the shaping process an aqueous emulsion containing an organopolysiloxane comprising 2 to 100 mol per cent of units of the general formula $R_xSiH_mO_{\frac{4-m-x}{2}}$, in which R represents an alkyl radical having 1 to 4 carbon atoms, x represents 0, 1 or 2, on average 0.7 to 1.3, m represents 1, 2 or 3 and the sum of $m + x$ is 1, 2 or 3, and 0 to 98 mol per cent of units of the general formula $R_nSiO_{\frac{4-n}{2}}$, in which R has the meaning given above and n represents 0, 1, 2 or 3, on average 0.9 to 1.8, the ratio of the sum of the silicon-bonded hydrogen atoms to the sum of the silicon atoms in the two kinds of silicon units being 0.02 to 1.25.

2. A process as claimed in claim 1, wherein at least 80% of the radicals R are methyl radicals.

3. A process as claimed in claim 1, or claim 2, wherein the average value of x is 0.9 to 1.0 and the average value of n is 0.9 to 1.2.

4. A process as claimed in any one of claims 1 to 3, wherein the ratio of the sum of silicon-bonded hydrogen atoms to the sum of silicon atoms in the two types of siloxane unit is 0.1 to 1.0.

5. A process as claimed in any one of claims 1 to 4, wherein the inorganic substance has a pH value below 7.5 in the aqueous medium prior to hardening.

6. A process as claimed in claim 5, wherein the inorganic substance is gypsum.

7. A process as claimed in claim 6, wherein the gypsum is in the form of plaster.

8. A process as claimed in claim 5, wherein the inorganic substance is a binder based on magnesium oxide and magnesium chloride.

9. A process as claimed in any one of claims 1 to 8, wherein the inorganic substance is used in the presence of conventional additives.

10. A process as claimed in any one of claims 1 to 9, wherein the shapes are made or coatings applied by the conventionally used methods.

11. A process as claimed in any one of claims 1 to 10, wherein the organopolysiloxane is a copolymer of siloxane units that contain no silicon-bonded hydrogen and siloxane units that contain silicon-bonded hydrogen.

12. A process as claimed in any one of claims 1 to 10, wherein the organopolysiloxane is a mixture of an organopolysiloxane that contains no silicon-bonded hydrogen and an organopolysiloxane that contains silicon-bonded hydrogen on some or all of the siloxane units.

13. A process as claimed in any one of claims 1 to 10, wherein the organopolysiloxane is an organopolysiloxane that contains silicon-bonded hydrogen in all the siloxane units.

14. A process as claimed in any one of claims 1 to 12, wherein the organopolysiloxanes that are free from silicon-bonded hydrogen contain not more than 25% of siloxane units having 2 or 3 silicon-bonded organo radicals per molecule and, in the water-free state, have a viscosity not exceeding 1000 cSt at 25°C (measured on a 50% by weight toluene solution).

15. A process as claimed in any one of claims 1 to 14, wherein 1 to 20— of the siloxane oxygen atoms of the organopolysiloxane have been replaced by hydroxyl groups and/or alkoxy groups of the formula —OR, where R is as defined in claim 1.

16. A process as claimed in any one of claims 1 to 15, wherein the organopolysiloxane has been prepared by the joint or separate hydrolysis of the corresponding halogenosilanes.

17. A process as claimed in any one of claims 1 to 16, wherein the aqueous emulsion of the organopolysiloxanes also contains a dispersing agent.

18. A process as claimed in claim 17, wherein the dispersing agent is a non-ionic dispersing agent.

19. A process as claimed in claim 17 or claim 18, wherein the dispersing agent is present in a proportion of 0.1 to 5% by weight, calculated on the organopolysiloxanes.

20. A process as claimed in any one of claims 1 to 19, wherein the emulsion is prepared from a solution of the organopoly-

siloxane in an organic solvent that is liquid under normal conditions.

21. A process as claimed in claim 20, wherein the organic solvent is used in a proportion of 25 to 75% by weight, calculated on the organopolysiloxane.

22. A process as claimed in claim 20 or claim 21, wherein the aqueous emulsion also contains the organic solvent.

23. A process as claimed in any one of claims 1 to 22, wherein the aqueous emulsion contains 0.001 to 50% by weight of organopolysiloxane.

24. A process as claimed in any one of claims 1 to 23, wherein the organopolysiloxane is used in a proportion of 0.001 to 10% by weight, calculated on the dry weight of the inorganic substance.

25. A process as claimed in claim 24, wherein the organopolysiloxane is used in a proportion of 0.02 to 2% by weight, calculated on the dry weight of the inorganic substance.

26. A process as claimed in any one of claims 1 to 25 wherein the organopolysiloxane emulsion is added to the mixing water added to the inorganic substance to effect hardening thereof.

27. A process as claimed in any one of claims 1 to 25, wherein the organopolysiloxane emulsion is used as the mixing water added to the inorganic substance to effect hardening thereof.

28. A process as claimed in claim 1, conducted substantially as described in any one of the Examples herein.

29. Water-repellent fabricated shaped structures and coatings whenever prepared by the process as claimed in any one of claims 1 to 28.

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